COLOUR AND CHEMICAL CONSTITUTION.

Part IV.—The Remaining Phthaleins.

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In continuation of the systematic examination of the absorption-spectra of the phthaleins described in the three earlier parts of this work (1917), I have now prepared the phthaleins of all the remaining phenolic substances which are obtainable or capable of being made in South Africa. The following are the data observed in these new substances:

A. Direct Substitution-products of Ordinary Phenolphthalein.

(1) *α-anthrol-phthalein*, from *α*-anthrol (Journ. Chem. Soc. Lond., 1916, p. 774) and phthalic anhydride, gives a brownish-green solution in alkali possessing an olive-green fluorescence. Its absorption-band is very near the red end, and can only be seen by use of direct sunlight, the centre being at about λ 740. In conc. H_2SO_4 the band is broader and has its centre about λ 720.

(2) *Phenol-α-anthrol-phthalein*, from anthrol and oxybenzoylbenzoic acid, gives a greenish-blue colour in alkali. The centre of the absorption-band is at λ 628. This substance is the (mono) xylylidene* derivative of phenolphthalein, and is interesting as showing the greatest displacement of the absorption-band observed (a diminution of frequency of 13 per cent. for the single C_8H_6 group which constitutes the difference between anthracene and benzene). In the case of phenol-*α*-naphtholphthalein the fall of frequency is 9·5 per cent. for the single butylidene group, which constitutes the difference between naphthalene and benzene. In conc. H_2SO_4 the above anthrol compound is purplish blue, with its band at λ 611.

(3) *Phenol metacresolphthalein* or *metamethyl-phenolphthalein* is purplish-pink in alkali, the band being at λ 569. In H_2SO_4 the colour is salmon and the band at λ 526. In connection with metacresolphthalein, described in Part I, I have now to issue a correction. The centre of its absorption-band as it λ 584, not λ 590. The specimen examined last year contained a trace of thymolphthalein, which caused a broadening of its band and a mis-estimate of its centre.

* Xylylidene is naphthalene minus CH·CH.

(4) *Phenolphthalein dimethyl ether.*—This long-known substance, which gives no colour in alkali, gives a salmon colour in H_2SO_4 with absorption-band centre at λ 508. Phenolphthalein monomethyl ether, examined in the same way, showed its band-centre to be at λ 503: that of phenolphthalein itself in H_2SO_4 is at λ 499.

(5) *Phenolphthalein monosuccinic acid*, made by condensing oxybenzoylbenzoic acid with *o*-oxyphenylsuccinic acid (itself made from coumarine), is purplish-pink in alkali with band-centre at λ 564. In H_2SO_4 it is salmon-coloured with band-centre at λ 502.

(6) *Phenolphthalein-disuccinic acid*, from the above acid with phthalic anhydride, could only be obtained in traces. Its band-centre in alkali is at λ 575, the displacement of the band from that of phenolphthalein being about twice that of the foregoing monosuccinic acid.

(7) *Thymolmetacresolphthalein.*—This substance, which is intermediate in constitution between *m*-cresol- and thymol-phthaleins, and thus enabled the influence of the *o*-isopropyl group to be studied, was made by condensing metacresol with a new acid, *thymoylbenzoic acid* (*2-methyl-5-isopropyl-4-oxybenzoylbenzoic acid*). The latter is made from thymolphthalein in the same way as oxybenzoylbenzoic acid is made from phenolphthalein (see Part II). This new phthalein is violet in alkali with its band-centre at λ 590 almost exactly across the **D** line of the solar spectrum. In H_2SO_4 it is pink with a broad band, the centre of which is at about λ 530.

(8) *Thymol-α-naphtholphthalein*, from α-naphthol and thymoylbenzoic acid, is bluish-green in alkali, the centre of its absorption-band being at λ 633. This forms an interesting example of the fact that the effects of the substitutions are additive, *i. e.* that the colour and position of the absorption-band of very complex phthaleins can be predicted from data obtained from simpler phthaleins. Thymolnaphtholphthalein can be looked on either as (*a*) thymolphenolphthalein, to which the butylidene group has been added (converting phenol into naphthol), or (*b*) as phenolnaphtholphthalein, to which the methyl and isopropyl groups have been added (converting phenol—in the other ring—into thymol). Now, in case (*a*) the value of the butylidene group can be ascertained by comparing the spectrum of phenol-α-naphtholphthalein with that of phenolphthalein. The central wave-lengths of these substances are 607 and 554, so that the single butylidene group which makes the difference between them has raised the wave-length of the band by 9·5 per cent. Applying, therefore, a correction of + 9·5 per cent. to the figure for phenol*thymol*phthalein (previously ascertained to be λ 578, see Part II), we get $1{\cdot}095 \times 578 = \lambda\,633$ as the calculated value for thymol-α-naphtholphthalein. In case (*b*), in the same way, we take the experimentally ascertained value for phenol*naphthol*-phthalein (viz. λ 607) and multiply it by the ratio indicating the conversion of one phenol group into a thymol group (viz. 1·044 or 578 ÷ 554), this

giving a second theoretical value for the band-centre in the supposed unknown thymolnaphtholphthalein, viz. 607 × 1·044 or λ 634.

The *observed* value being λ 633, it is seen that both predictions are accurate.

(9) *Thymol-α-anthrolphthalein*, from thymoylbenzoic acid and α-anthrol, is bluish-olive in alkali with an indefinite spectrum consisting of a strong dulling of the yellowish-green and the outer red. The centre of the latter band is probably λ 710, and the other may be due to the presence of a little thymolphthalein. In H_2SO_4 the colour is emerald and the absorption-band sharp with centre at λ 636.

(10) *Monophenyl ether of phenolphthalein.*—An attempt to make this substance from oxybenzoylbenzoic acid and $(C_6H_5)_2O$ using H_2SO_4 as condensing agent gave a product which was mostly composed of phenolphthalein, but also contained another substance having a broad band with centre at λ 470. It is quite probable that the latter substance is merely β-oxyanthraquinone (see Part III), the absorption-band of which was observed to be at λ 475 (α-oxyanthraquinone has its band-centre at λ 490).

Secondary bands of the phthaleins.—The existence of an absorption-band possessing $\frac{2}{3}$ of the wave-length and $\frac{3}{2}$ of the frequency of the visible band having been suspected (and indicated in Part I), an examination of the extreme violet end was attempted. Lack of quartz apparatus prevented the application of the photographic method. It was found that strong solution of alkaline phenolphthalein absorbs the extreme violet, the *edge* of the band coming up to λ 380, which is consistent with the presence of a band with its centre at $\frac{2}{3}$ × 554 or λ 369. In the case of thymolphthalein in strong solution in alkali the absorption of the violet is almost total, the edge of the absorption extending to λ 420 ($\frac{2}{3}$ × 597 = λ 398 calculated for centre).

B. Derivatives of *o-p*-phenolphthalein.

(*a*) *Phenolquinolphthalein.*—This is obtained as usual from oxybenzoylbenzoic acid and quinol, but purification of the product was unsuccessful, and since the absorption-band is vague, no further investigation was made. The colour of the phthalein in alkali is maroon: band-centre about λ 540, *i.e.* lower than that of any of the para-phthaleins. In H_2SO_4 the phthalein gives a yellow solution, the band being extremely far down in the blue, at about λ 435—a position similar to that of fluoresceine in H_2SO_4.

(*b*) *Ethyl ether of foregoing phthalein.*—This was obtained by using EtO⟨⟩OH (from phenetidine) instead of quinol. The product was also unsatisfactory. The alkaline colour is dirty purple with a very broad band at about λ 552 and signs of another at about λ 490.

(*c*) *Thymol*-p-*ethoxyphenol-phthalein* from EtO⟨⟩OH and thymoyl-

benzoic acid is blue in alkali with central wave-length at λ 598. It differs from thymolphthalein in giving an orange solution in H_2SO_4 in which there is no band at λ 550, the absorption being in the violet.

(*d*) *Thymol*-p-*cresol-phthalein* also resembles thymolphthalein in alkaline solution, its central wave-length being at about λ 595; in H_2SO_4 it is also orange (thymolphthalein purplish-pink) with only violet-absorption. The additive property may again be illustrated here:

$$\frac{\text{phenolparacresolphthalein}}{\text{phenolphthalein}} = \frac{572}{554}, \text{ and } \frac{\text{phenolthymolphthalein}}{\text{phenolphthalein}} = \frac{578}{554}$$

$$\therefore \text{ calculated value for thymol-}p\text{-cresol-phthalein is } \frac{572 \times 578}{554} = 597.$$

The agreement is better if the *differences* are merely added together: 572 + 578 − 554 = 596.

(*e*) *Thymol-β-naphtholphthalein* is also indefinite: it is bluish-green in alkali with absorption-centre about λ 700, and like the rest of the class is orange in H_2SO_4 with violet absorption and no fluorescence.

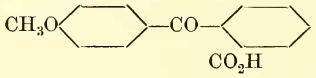
(*f*) *Phenol-β-anthrolphthalein* is olive-green in alkali with a band at the treme red: its centre is about λ 730.

c. Derivatives of Phenylphenolphthalein (Oxydiphenylphthalide).

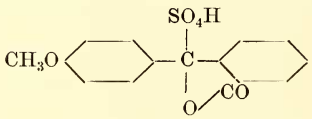
Phenylmetacresolphthalein.—Condensation of benzoylbenzoic acid with metacresol yielded a phthalein which, although giving a salmon colour in H_2SO_4 (central-wave-length λ 506), gave a perfectly colourless solution in alkali whatever strength of the latter was used. To explain this is difficult: one can only assume that since oxydiphenylphthalide itself is *easily* bleached by excess alkali, the methyl group in the new substance has so exaggerated this property that the quinonoid phase only exists momentarily, passing immediately into the colourless carbinol phase.

Phenylparacresolphthalein and *phenylparaoxybenzoic-acid-phthalein* were both yellowish-orange in alkali. The former had no band and the latter a faint, broad one at about λ 486.

The absorption-band of the orange H_2SO_4 solution of *anisoylbenzoic acid*



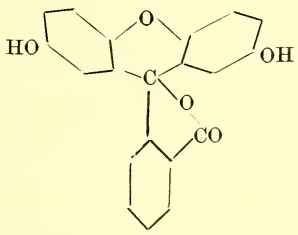
was observed to be at λ 466 about 7 units higher than that of the unmethylated substance (Part II). These almost unique sharp bands in the blue are due to the formation of phthalein-like sulphates, thus—



Similarly, the absorption-band of xanthone, the simplest fluorescent substance, in H_2SO_4 was found to be at λ 410.

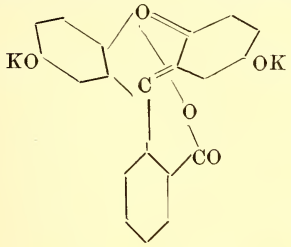
Note on the guaiacol-phthaleins.—It having been recently shown that when guaiacol is brominated the bromine does not enter *para* to the — OH but is *para* to the — OCH_3 group (Journ. Chem. Soc., Lond., 1917, p. 941), it becomes probable that guaiacolphthalein and phenolguaiacolphthalein also have the methoxyl group *para* to the central-linking carbon, and consequently have the free — OH group of guaiacol *meta* to this carbon. Experiment confirmed this, for when 5-bromoguaiacol was condensed with oxybenzoylbenzoic acid and H_2SO_4 at a low temperature, the phthalein produced was phenolguaiacolphthalein, bromine having been eliminated. This could scarcely be imagined unless the linkage to a phthalein occurred at the same point as the bromine came off at. The dibromoguaiacolphthalein described in Part I, obtained by direct bromination, has, therefore, probably one bromine in each ring *ortho* to the — OH groups and also *ortho* to the central carbon.

Note on quinolphthalein.—The ordinary formulation of this substance:

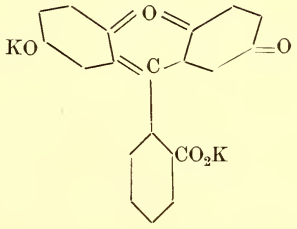


is not quinonoid and does not account for its colour.

The present writer now suggests two (tautomeric) formulae for the salts of this substance, which are quinonoid.



and



These two formulae are almost identical when it is considered that the K atoms are ionised off the molecule.

Some General Quantitative Conclusions on the Effect of Substitutions on Phenolphthalein.

One *o*-methyl	group	raises	the absorption wave-length by	1·5	per cent.
Two „	groups	raise	„ „ „	2·9	„
One *m*-methyl	group	raises	„ „ „	2·7	„
Two „	groups	raise	„ „ „	5·5	„
One *o*-isopropyl	group	raises	„ „ „	1·3	„ (?)
Two „	groups	raise	„ „ „	2·4	„
One *m*-isopropyl	group	raises	„ „ „	3·0	„
Two „	groups	raise	„ „ „	5·6	„
Replacement of phthalic CO by SO_2		raises	„ „ „	1·4	„
Two *o*-Br atoms		raise	„ „ „	1·7	„
Four „ „		„	„ „ „	5·0	„
Four *o*-I „		„	„ „ „	6·0	„
The oxygen "oxo"-linkage in fluorescein		depresses	„ „ „	10·0	„

There are many other additive relationships which are, however, less regular than these, possibly owing to difficulties of observation only.